

# Three-photon detachment of electrons from the fluorine negative ion

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**Abstract.** Absolute three-photon detachment cross sections are calculated for the fluorine negative ion within the lowest-order perturbation theory. The Dyson equation of the atomic many-body theory is used to obtain the ground-state  $2p$  wavefunction with correct asymptotic behaviour, corresponding to the true (experimental) binding energy. We show that in accordance with the adiabatic theory (Gribakin and Kuchiev 1997 *Phys. Rev. A* **55** 3760) this is crucial for obtaining absolute values of the multiphoton cross sections. Comparisons with other calculations and experimental data are presented.

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## 1. Introduction

Starting from the pioneering works of Hall *et al* (1965) and Robinson and Geltman (1967) the behaviour of negative ions in laser fields has been the subject of numerous studies for over thirty years. Nevertheless, up to now there are very few firmly established results on the absolute values of the cross sections and photoelectron angular distributions in multiphoton processes.

This is true even for the simplest two-photon detachment processes. For example, the results of a number of experimental and theoretical works on the cross sections and photoelectron angular distributions in the negative halogen ions (see, e.g., van der Hart 1996, Gribakin *et al* 1999 and references therein) differ significantly each from other. A number of experimental works reported the cross sections and angular asymmetry parameters of the two-photon detachment from the halogen negative ions at selected photon energies (Trainham *et al* 1987, Blondel *et al* 1989a, 1992, Kwon *et al* 1989, Davidson *et al* 1992, Sturru *et al* 1992, Blondel and Delsart 1993). These measurements were performed at the end of 80's – beginning of 90's, and to the best of our knowledge no new experimental data on multiphoton detachment from the negative halogens have been published since.

On the theoretical side, a recent development in the study of multiphoton detachment from negative ions has been done within the adiabatic approach (Gribakin and Kuchiev 1997a,b). It has established that the electron escape from an atomic system in a low-frequency laser field takes place at large electron-atom separations,

$$r \sim 1/\sqrt{\omega} \sim \sqrt{2n}/\kappa \gg 1, \quad (1)$$

where  $\omega$  is the photon frequency,  $\kappa$  is related to the initial bound-state energy,  $E_0 = -\kappa^2/2$ , and  $n$  is the number of quanta absorbed (atomic units are used throughout). Therefore, the asymptotic behaviour of the bound-state wavefunction  $R(r) \simeq Ar^{-1}e^{-\kappa r}$  is crucial for obtaining correct absolute values of the probabilities of multiphoton processes. Direct calculations of two-photon detachment from halogen negative ions within the lowest-order perturbation theory (Gribakin *et al* 1998, 1999) with both the Hartree-Fock (HF) and the asymptotically correct valence  $np$  wavefunctions confirm this understanding. The point is that the HF wave functions are characterised by  $\kappa$  values generally exceeding the true experimental ones. As a result, when we use asymptotically correct wave functions the cross sections are significantly higher than those obtained within other methods which rely on the HF or similar ground-state wavefunctions (Crance 1987, 1988, Jiang and Starace 1988, Pan *et al* 1990, van der Hart 1996). Moreover, the use of the ground-state wavefunctions with correct asymptotic behaviour in multiphoton detachment calculations is often more important than other effects of electron correlations. Note that the analytic adiabatic theory (Gribakin and Kuchiev 1997a,b) which is valid for  $n \gg 1$  gives reasonable estimates of the cross sections

even for  $n = 2$  when correct asymptotic parameters are used.

As far as three-photon detachment from negative ions is concerned, the experimental and theoretical results are more scarce than those on the two-photon detachment. Thus, there have been only two experimental measurements of the cross section for  $F^-$  at a single photon energy performed by Blondel *et al* (1989b) and Kwon *et al* (1989), and a few theoretical values obtained in the early calculations by Crance (1987, 1988). Recently van der Hart (1996) applied an  $R$ -matrix Floquet approach to study the photodetachment from  $F^-$  and  $Cl^-$  for  $n = 1, 2$  and 3.

The aim of this work is to perform direct numerical calculations of the three-photon detachment cross section for the negative fluorine ion using an asymptotically correct ground-state wavefunction and compare the results with the available theoretical and experimental data. As in our previous two-photon calculations (Gribakin *et al* 1999) the correct  $2p$  wavefunction is obtained within the many-body Dyson equation method. Section 2 outlines briefly the method of calculation. A discussion of our results and comparisons with other calculations and experimental data are presented in Section 3.

## 2. Three-photon detachment cross section

The total cross section of three-photon detachment of the  $n_0 l_0$  electron from an atomic system by a linearly polarized light of frequency  $\omega$  can be written as

$$\sigma(\omega) = \sum_{l_f, L} \sigma_{l_f L} = \frac{32\pi^4 \omega^3}{c^3} \sum_{l_f, L} \left| B_{l_0, l_f}^{(L)}(\omega) \right|^2. \quad (2)$$

In this sum above the partial cross sections  $\sigma_{l_f L}$  are characterised by the orbital momentum  $l_f$  of the final-state photoelectron coupled with the atomic residue into the total orbital momentum  $L$ . The second equality assumes that the continuous-spectrum wavefunction of the photoelectron in the matrix element  $B_{l_0 l_f}^{(L)}(\omega)$  is normalized to the  $\delta$ -function of energy. After absorption of three dipole photons by an outer  $np$  electron in a halogen negative ion  $np^6 \ ^1S$ , the final state photoelectron can leave the system in the  $s$ -,  $d$ - or  $g$ -waves. So, the possible final states are:  $l_f = 0$  ( $^1P$ ),  $l_f = 2$  ( $^1P$  and  $^1F$ ) and  $l_f = 4$  ( $^1F$ ).

In the lowest perturbation-theory order the three-photon amplitude  $B_{l_0 l_f}^{(L)}(\omega)$  is characterised by the following sequence of electronic states,  $n_0 l_0(L_0) \rightarrow n_1 l_1(L_1) \rightarrow n_2 l_2(L_2) \rightarrow E_f l_f(L)$ , produced by successive absorption of three photons. This amplitude may be presented as

$$\begin{aligned} B_{l_0 l_f}^{(L)} &= \sum_{L_2 l_2} \sqrt{(2L_2 + 1)(2L + 1)} \begin{pmatrix} 1 & L & L_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1 & L & L_2 \\ l_0 & l_2 & l_f \end{Bmatrix} \\ &\times \sum_{E_2} \frac{\langle \varepsilon_f l_f \parallel \hat{d} \parallel n_2 l_2 \rangle A_{l_0 l_2}^{L_2}(\omega, E_0, E_2)}{2\omega - E_2 + E_0 + i\delta}, \end{aligned} \quad (3)$$

where  $n_2l_2$  is the intermediate electron state after the absorption of the second photon,  $l_2$  is the electron's orbital momentum and  $L_2$  is the total orbital momentum of the system in the intermediate state. For a halogen negative ion  $l_2 = 1$  with  $L_2 = 0, 2$  and  $l_2 = 3$  with  $L_2 = 2$ . In equation (3) and below  $E_0$ ,  $E_1$ ,  $E_2$ , and  $E_f$  are energies of the corresponding electron states. The amplitude  $A_{l_0l_2}^{L_2}(\omega, E_0, E_2)$  in equation (3) is the two-photon amplitude (cf. Pan *et al* 1990, Gribakin *et al* 1999),

$$A_{l_0l_2}^{L_2}(\omega, E_0, E_2) = \sqrt{2L_2 + 1} \begin{pmatrix} 1 & L_2 & 1 \\ 0 & 0 & 0 \end{pmatrix} \sum_{l_1} (-1)^{l_1} \begin{Bmatrix} 1 & 1 & L_2 \\ l_2 & l_0 & l_1 \end{Bmatrix} M_{l_0l_1l_2}^{L_2}(\omega, E_0, E_2), \quad (4)$$

where the two-photon radial matrix element  $M_{l_0l_1l_2}^{L_2}(\omega, E_0, E_2)$  is given by

$$M_{l_0l_1l_2}^{L_2}(\omega, E_0, E_2) = \sum_{E_1} \frac{\langle n_2l_2 || \hat{d} || n_1l_1 \rangle \langle n_1l_1 || \hat{d} || n_0l_0 \rangle}{\omega + E_0 - E_1 + i\delta}. \quad (5)$$

The sums in equations (4) and (5) run over the intermediate electron states  $n_1l_1$  populated after the absorption of the first photon ( $l_1 = 0, 2$  with  $L_1 = 1$  for the halogen negative ions). The reduced dipole matrix elements are defined in the usual way, e.g., in the length form,

$$\langle nl || \hat{d} || n_0l_0 \rangle = (-1)^{l_>} \sqrt{l_>} \int P_{nl}(r) P_{n_0l_0}(r) r dr, \quad (6)$$

where  $l_> = \max\{l, l_0\}$  and  $P$ 's are the radial wave functions.

If one describes the initial state  $n_0l_0$  in the HF approximation, the asymptotic behaviour of the corresponding radial wavefunction is incorrect. Namely, it is characterized by  $\kappa$  corresponding to the HF binding energy, rather than the exact (experimental) one. Thus, in  $F^-$  the HF value is  $\kappa = 0.6$ , whereas the true one is  $\kappa = 0.5$ . As we showed for the two-photon detachment (Gribakin *et al* 1998, 1999), it is very important to use asymptotically correct bound-state wavefunctions. In the present work we refine the bound-state wavefunction using the Dyson equation method in the same way as it was done in our two-photon calculations (Gribakin *et al* 1999). This enables us to obtain the  $2p$  wavefunction of  $F^-$  with the correct binding energy  $|E_{2p}| = 0.250$  Ryd, equal to the electron affinity of fluorine (Hotop and Lineberger 1985).

The wavefunctions of the intermediate ( $n_1l_1, n_2l_2$ ) and final ( $E_f l_f$ ) states of the photoelectron are calculated in the HF field of the frozen neutral F-atom residue  $2p^5$ . The photoelectron is coupled to the atomic residue to form the total spin  $S = 0$  and the angular momenta  $L_1 = 1$  for the first intermediate  $s$  and  $d$  states ( $l_1 = 0, 2$ ),  $L_2 = 0, 2$  for the second intermediate  $p$ -wave state ( $l_2 = 1$ ), and  $L_2 = 2$  for the second intermediate  $f$ -wave state ( $l_f = 3$ ). In the final state the photoelectron is coupled to the core with  $L_f = 1$  for the  $s$ - and  $d$ -wave, and  $L_f = 3$  for the  $d$ - and  $g$ -wave. The intermediate state continua are discretized and represented by a 70-state photoelectron momentum mesh with constant spacing  $\Delta k$ .

Note that the importance of large distances in multiphoton problems speaks in favour of the length form of the photon dipole operator (Gribakin and Kuchiev 1997a,b). This is in agreement with the results of Pan *et al* (1990) who showed that the two-photon detachment cross sections obtained with the dipole operator in the velocity form are much more sensitive to the shift of the photodetachment threshold and correlation corrections. On the other hand, electron correlations have a much weaker effect on the calculations with the length form, and the corresponding results are more robust, and hence, more reliable.

The two-photon  $A_{i_0 i_2}^{L_2}(\omega, E_0, E_2)$  (4) and three-photon  $B_{i_0 i_f}^{(L)}(\omega)$  (3) amplitudes are calculated by direct summation over the intermediate states. This method involves accurate evaluation of the free-free dipole matrix elements, and special attention is paid to pole- and  $\delta$ -type singularities of the integrand (Korol 1994, 1997).

### 3. Results

In the present work we demonstrate the effect of the asymptotic behaviour of the bound-state wavefunction by presenting the results obtained with the HF  $2p$  wavefunction ( $E_{2p}^{\text{HF}} = -0.362$  Ryd), and with the  $2p$  wavefunction which possesses a correct experimental energy  $E_{2p}^{\text{exp}} = -0.250$  Ryd. The latter is obtained within the Dyson equation approach (Gribakin *et al* 1999). It is quite close to the HF wavefunction inside the atom, whereas for  $r > 2$  au it has larger values than the HF solution, due to a smaller binding energy and  $\kappa$ . The asymptotic behaviour of the Dyson  $2p$  orbital is characterized by  $\kappa = 0.5$  and  $A = 0.64$ . For comparison we also calculate the cross sections within the plane-wave approximation and using the analytic adiabatic theory formula (Gribakin and Kuchiev 1997a,b).

In figure 1 we present three-photon detachment cross sections calculated for  $\text{F}^-$  using various approaches for the whole energy range studied. Figure 2 shows a comparison between our results and other theoretical and experimental results. In general, all calculations reveal the small near-threshold maximum due to the contribution of the final photoelectron  $s$ -wave, and a broad maximum at larger energies due to the  $d$ -wave contribution.

When we use the experimental threshold energy together with the HF  $2p$  wavefunction (double-dot-dash curve in figure 1), the overall magnitude of the cross section remains close to that obtained with the HF threshold and wave function. On the other hand, when we use the  $2p$  Dyson orbital (solid line) the cross section becomes substantially higher. This clearly demonstrates the effect of the asymptotic behaviour of the bound-state wavefunction. Moreover, the difference between the three-photon cross sections obtained with the HF and Dyson  $2p$  wavefunctions is greater than that between the corresponding two-photon cross sections (Gribakin *et al.* 1999). This can

be related to the fact that with the increase of  $n$  the range of important distances (1) increases, and the difference between the two bound-state wavefunctions becomes more significant.

The cross section obtained using the HF  $2p$  orbital together with the experimental  $2p$  energy (double-dot-dash line in figures) shows a maximum of  $\sigma = 12.5$  au at  $\omega = 0.125$  Ryd, near the two-photon detachment threshold. The HF results of Crance (1987) below the two-photon detachment threshold (solid squares in figure 2) are close to ours. The cross section of van der Hart (1996) obtained within the  $R$ -matrix Floquet approach is 20–30% higher (dashed line in figure 2) with a maximum of  $\sigma = 14.5$  au at  $\omega = 0.111$  Ryd. Note that a similar difference between the HF calculations with the experimental energy and the  $R$ -matrix Floquet approach was found for the two-photon detachment cross sections of  $F^-$  and  $Cl^-$  (Gribakin *et al* 1999). It may be due to the fact that some correlations are included in the  $R$ -matrix Floquet ground-state wavefunction (see discussion at the end of this section). The experimental results are shown in figure 2 by open symbols. Blondel *et al* (1989b) and Kwon *et al* (1989) have obtained the cross section values of  $\sigma = 4.75^{(+2.02)}_{(-1.40)}$  au and  $\sigma = 6.15^{(+5.14)}_{(-2.80)}$  au, respectively, at  $\omega = 0.0856$  Ryd. Taken with the error bars, the latter value is consistent with the HF and  $R$ -matrix Floquet calculation.

However, the best results of the present paper, shown by a solid curve in figure 2, indicate that the cross section is substantially larger. Let us repeat once more that this increase of the cross section is due to the events which happen at large separations, where all correlation corrections are controlled very well. Henceforth we believe that our calculations (solid curve) give the most accurate values for the cross section. Our cross section substantially, by a factor of 2, exceeds the HF results as well as the  $R$ -matrix Floquet result. It has a maximum of  $\sigma = 27$  au at  $\omega \approx 0.114$  Ryd. As is seen from figure 1, the difference between the cross sections obtained with the Dyson and HF orbitals decreases towards the one-photon detachment threshold ( $\omega = 0.25$  Ryd). Indeed, with the increase of  $\omega$  and the energy of the photoelectron, smaller distances become more important, see (1), and at these distances the two bound-state wavefunctions are quite close.

As noted above, the strong enhancement of the three-photon cross section due to a changed asymptotic behaviour of the wavefunction is in a agreement with the two-photon calculations (Gribakin *et al* 1998, 1999) and with the conclusions of the analytical adiabatic theory (Gribakin and Kuchiev 1997a,b). To make a direct comparison with this theory we calculate the cross section given by equation (5) of Gribakin and Kuchiev (1997b). The short-dash curve (figure 1) is obtained using  $A$  and  $\kappa$  values of the HF  $2p$  orbital. The corresponding cross section is rather close to the HF result (dashed curve) shifted to the HF threshold. When we use  $A$  and  $\kappa$  from the Dyson orbital, dot-dash curves in figures 1 and 2, the cross section becomes much higher. It is about 30%

greater than our direct perturbation-theory calculation with the Dyson orbital, which is a good accuracy for a simple analytical formula. If we describe the photoelectron in the intermediate and final states using plane waves instead of the HF wavefunctions the direct calculation (dotted line in figure 1) is very close to the adiabatic theory result. Therefore, we can attribute the discrepancy between the adiabatic theory and numerical calculations to the use of free-electron Volkov states in the theory. However, this discrepancy is not large, and it gets smaller with the increase of  $n$ .

We see that the use of the asymptotically correct  $2p$  wavefunction changes the three-photon detachment cross section by a factor of two or more. This is similar to the two-photon detachment process, where the effect described above is greater than other correlation effects (Pan *et al* 1990, Gribakin *et al* 1999). There is no reason to expect that the role of such correlations in three-photon detachment is stronger than in two-photon detachment. Thus, we conclude that in *multiphoton* processes the error introduced by using a bound-state wavefunction with incorrect asymptotic behaviour could be much greater than the effects of electron correlations. For the sake of pure terminology we should mention that the correct description of the asymptotic behaviour of a ground-state wave function needs inclusion of many-electron correlations, see the Dyson equation discussed above. However, these correlations are very particular, their manifestation can be described as a simple shift of the single-electron energy. In contrast, conventionally the term 'many-electron correlations' includes also processes which *cannot* be described in the single-electron picture. The later ones are *less important* in the problem considered.

#### 4. Concluding remarks

In the present paper we have performed direct numerical calculations of the three-photon detachment from the fluorine negative ion, and paid special attention to a proper description of the initial ground-state wavefunction. We ensured that it has correct asymptotic behaviour by calculating the outer  $2p$  orbital of the negative ion from the many-body theory Dyson equation with the non-local correlation potential adjusted to reproduce experimental binding energies. Our calculations demonstrate explicitly that the use of asymptotically correct initial state wavefunctions is very important for finding absolute values of multiphoton detachment cross sections. This confirms the conclusion of the adiabatic theory (Gribakin and Kuchiev 1997a,b, Gribakin *et al* 1999) about the significance of large electron-atom separations in multiphoton processes.

## 5. Acknowledgments

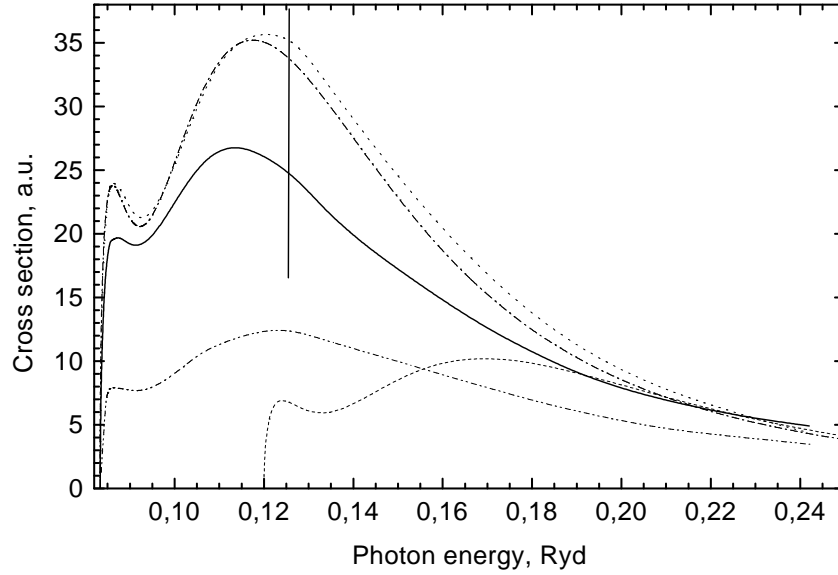
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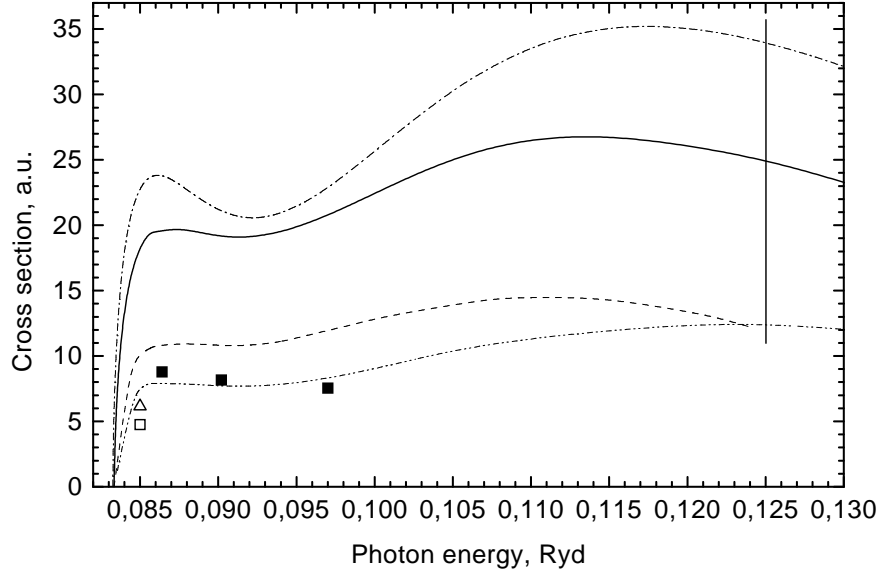
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## Figure captions



**Figure 1.** Three-photon detachment cross sections of  $F^-$ . Present calculations: - - -, and — · —, adiabatic theory, equation (5) of Gribakin and Kuchiev (1997b), with parameters corresponding to the HF  $2p$  wavefunction and to the corrected  $2p$  wavefunction, respectively; — · · —, direct calculation using the HF wavefunctions of the  $2p$ , intermediate and final states and experimental  $2p$ -energy; —, same with the  $2p$  wavefunction from the Dyson equation; · · · · ·,  $2p$  wavefunction from the Dyson equation and plane waves for the intermediate and final states. Vertical line shows the position of the two-photon detachment threshold.



**Figure 2.** Three-photon detachment cross sections of  $F^-$  from different calculations and experiment. Present calculations:  $-\cdot-$ , analytical adiabatic theory (Gribakin and Kuchiev 1997a,b) with parameters corresponding to the corrected  $2p$  wavefunction;  $-\cdot\cdot-$ , direct calculation using the HF wavefunctions of the  $2p$ , intermediate and final states and experimental  $2p$ -energy;  $---$ , same with the  $2p$  wavefunction from the Dyson equation. Other results:  $\blacksquare$ , HF calculation of Crance (1987);  $----$ ,  $R$ -matrix Floquet approach (van der Hart 1996);  $\square$ , and  $\triangle$  experiment Blondel *et al* (1989b) and Kwon *et al* (1989), respectively. Vertical line shows the position of the two-photon detachment threshold.